Electronic Supplementary Information

Self-supported formation of hierarchical $NiCo_2O_4$ tetragonal microtubes with enhanced electrochemical properties

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Experimental Section:

Preparation of $NiCo_2O_4$ Microtubes: In a typical synthesis, 0.5 mmol of $Ni(Ac)_2 \cdot 4H_2O$ and 1 mmol of $Co(Ac)_2 \cdot 4H_2O$ were dissolved into 3 ml of 1,3-propanediol completely. Then, 47 ml of isopropanol (IPA; Merck, 99.8%) was added into the above solution to form a pink solution. Thereafter, the resulting mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 160 ^oC for 12 h. After cooling to room temperature naturally, the precipitate was separated by centrifugation, washed with ethanol for several times and dried in an oven at 70 ^oC for 12 h. Finally, the as-prepared precursor was calcined at 300 ^oC in air for 2 h with a ramping rate of 2 ^oC min^{-1} to obtain $NiCo_2O_4$ microtubes. As a reference, the hierarchical nanoflowers were synthesized by increasing the amount of 1,3-propanediol to 10 ml (isopropanol: 40 ml) with other conditions unchanged.

Materials Characterization: The morphology and structure of the products were characterized using transmission electron microscopy (TEM; JEOL, JEM-2010), and field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F) equipped with an energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) patterns were collected on a Bruker D2 Phaser X-Ray Diffractometer with Ni filtered Cu *Kα* radiation (λ = 1.5406 Å) at a voltage of 30 kV and a current of 10 mA. X-ray photoelectron spectroscope (XPS) measurements were performed on a VG ESCALAB MKII X-ray photoelectron spectrometer. All of the binding energies (BEs) in this XPS analysis were corrected for specimen charging with reference to the C 1s peak (set at 284.6 eV). Thermogravimetric analysis (TGA) was performed on SDT Q600 (TA Instruments). The nitrogen sorption measurement was carried out on Autosorb 6B at liquid nitrogen temperature.

Electrochemical Measurements: The working electrode consists of active material, carbon black (Super-P-Li), and polymer binder (polyvinylidene fluoride; PVDF) in a weight ratio of 70:20:10. The slurry was pasted onto commercial nickel foam and then dried at 120 ^{o}C overnight under vacuum. The electrochemical tests were conducted with a CHI 660D electrochemical workstation in an aqueous 2.0 M KOH electrolyte with a three-electrode cell, where Pt foil serves as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The loading mass of $NiCo_2O_4$ microtubes on nickel foam was about 1.0 mg cm^{-2}. It should be pointed out that the capacitance of the electrode was calculated by the formula, $C = I\Delta t/\Delta V$, where C, I, Δt and ΔV are the specific capacitance (F g^{-1}) of the electroactive materials, the discharge current density (A g^{-1}), the discharge time (s), and the discharging potential range (V), respectively. Electrochemical impedance spectroscopy (EIS) measurement was carried out by applying an AC voltage with 1 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at open circuit potential.

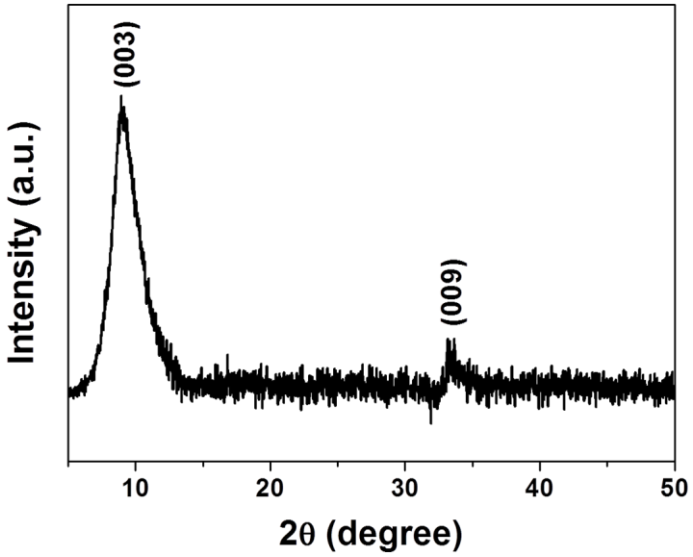

Fig. S1 XRD pattern of the as-prepared hierarchical NiCo-LDH tetragonal microtubes.

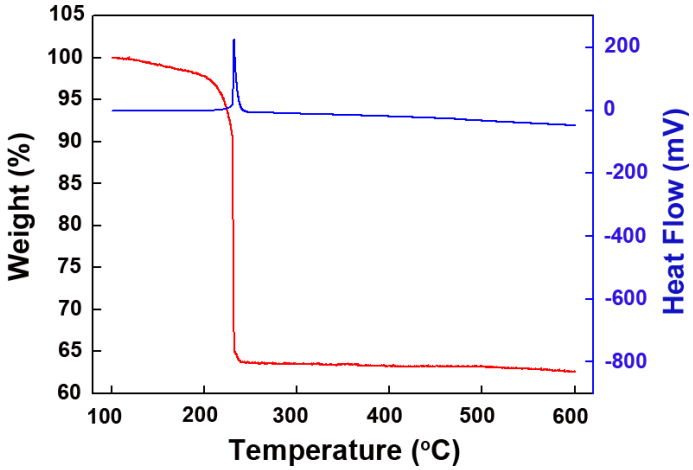

Fig. S2 TGA-DSC curve of as-prepared hierarchical NiCo-LDH tetragonal microtubes with a heating rate of 5 ^{o}C min^{-1} from 100 ^{o}C to 600 ^{o}C.

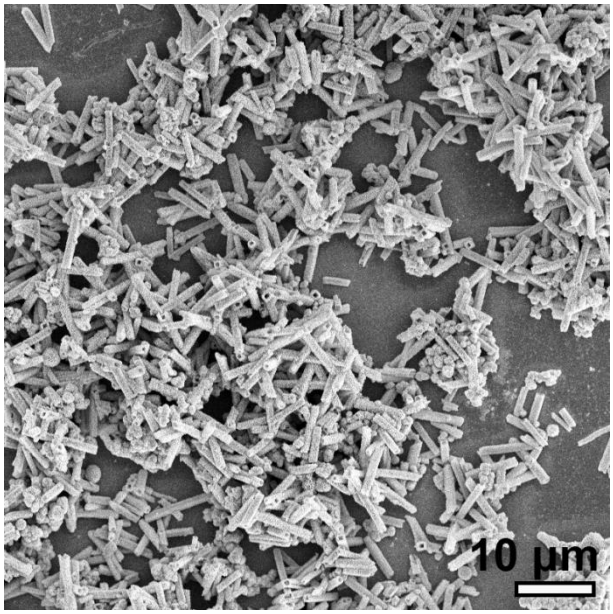

Fig. S3 Low-magnification FESEM image of as-prepared hierarchical $NiCo_2O_4$ tetragonal microtubes.

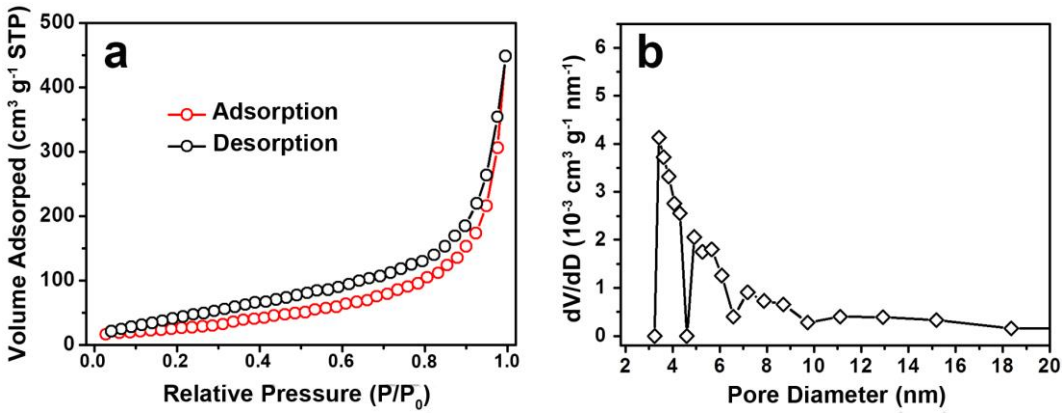

Fig. S4 (a) N_2 adsorption-desorption isotherms and (b) the corresponding pore size distribution of as-prepared hierarchical $NiCo_2O_4$ tetragonal microtubes.

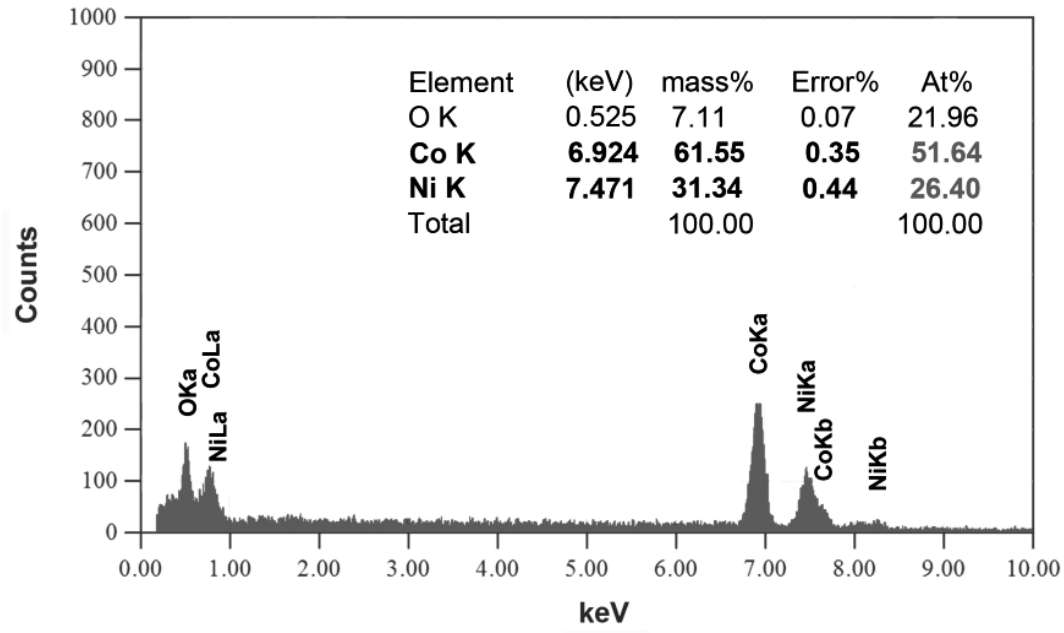

Fig. S5 EDX result of the as-prepared hierarchical $NiCo_2O_4$ tetragonal microtubes.

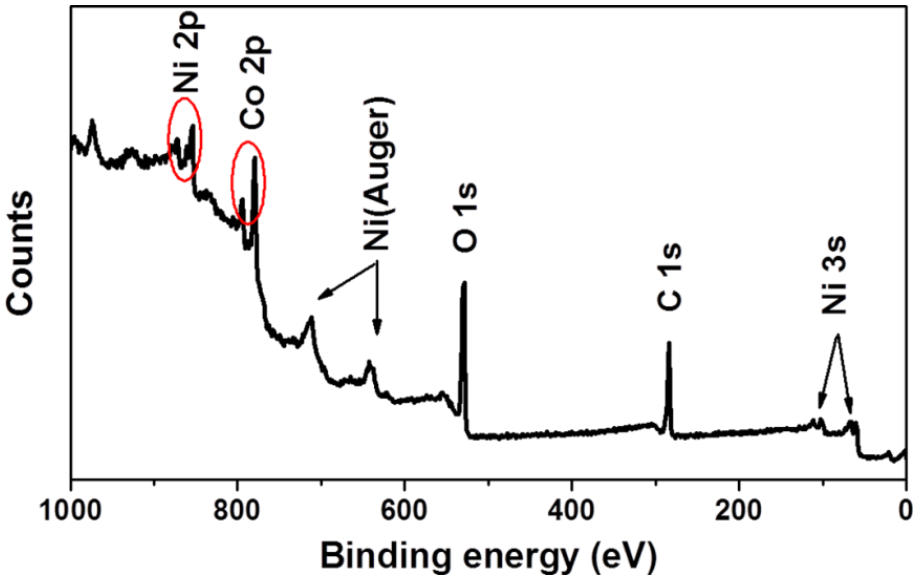

Fig. S6 XPS spectrum of the as-prepared hierarchical $NiCo_2O_4$ microtubes.

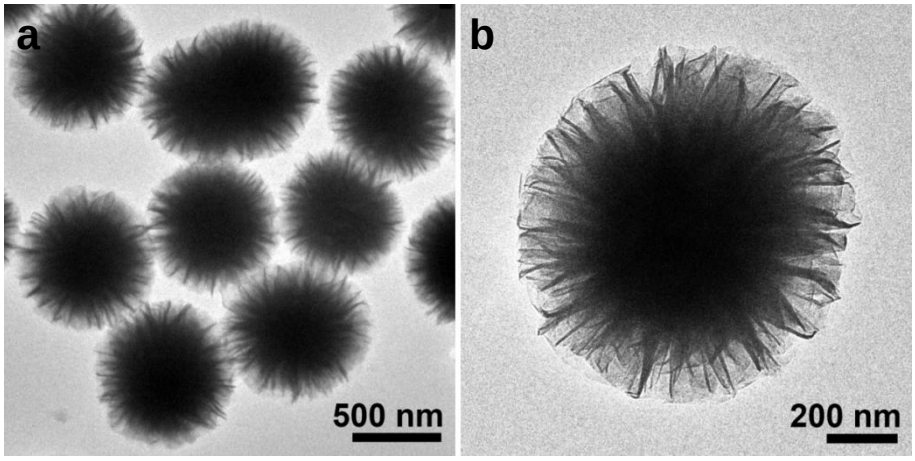

Fig. S7 TEM images of as-prepared hierarchical Ni-Co precursor nanoflowers with 10 ml of 1,3-propanediol added.

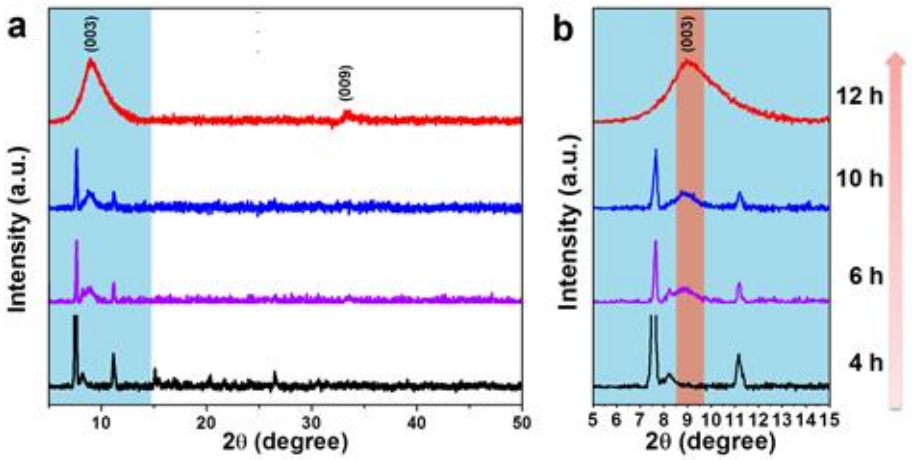

Fig. S8 (a) XRD patterns and (b) the magnified peaks of the as-obtained products with different reaction times.

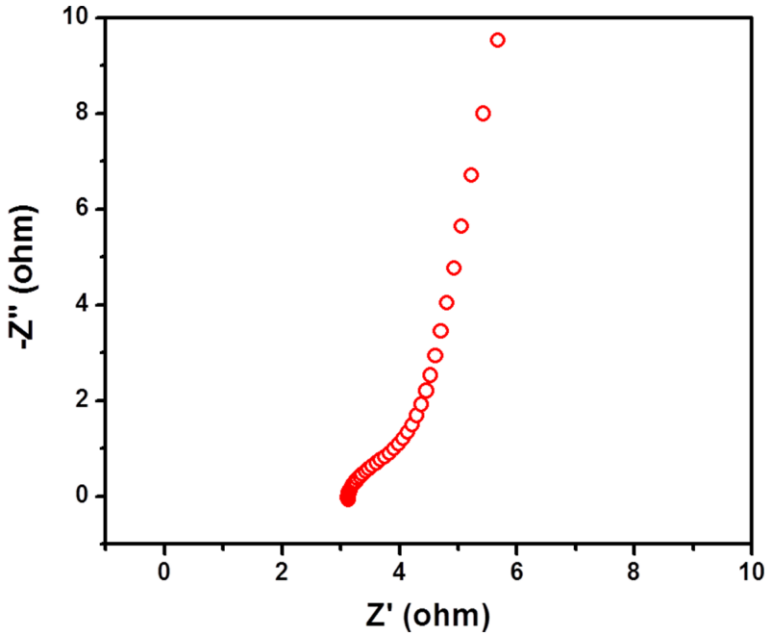

Fig. S9 EIS spectrum of the as-prepared hierarchical $NiCo_2O_4$ microtubes. In the high frequency region, the intersection of the curve at the real part indicates the resistance of the electrochemical system (R_s). The small value confirms the good bulk conductivity of the $NiCo_2O_4$ sample. Meanwhile, the small semicircle and ideal straight line along the imaginary axis in the low frequency regime correspond to the much low charge-transfer resistance at the electrode/electrolyte interface and the low diffusion resistance.

Table S1. Comparison of electrochemical performance of hierarchical $NiCo_2O_4$ tetragonal microtubes with some representative $NiCo_2O_4$ nanostructures

$NiCo_2O_4$ based nanostructures	**Loading mass (mg/cm^{-2})**	**Specific capacitance ($F\ g^{-1}$)**	**Stability**	**Ref.**
Hierarchical $NiCo_2O_4$ microtubes	~1.0	1180.1 (10 A g^{-1})	89.4 % 12000 cycles	This work
$NiCo_2$-DH/$NiCo_2O_4$ nanoarrays	~1.0	~1640 (2 mA cm^{-2})	82.3% 2000 cycles	10
$NiCo_2O_4$ double-shell hollow spheres	4	568 (1 A g^{-1})	85.8% 2000 cycles	34
Mesoporous $NiCo_2O_4$ nanowire arrays	~1.2	1102 (8 A g^{-1})	~100% 5000 cycles	35
$NiCo_2O_4$ nanosheets on Ni wires	Not reported	10.3F cm^{-3} (0.08 mA)	78% 5000 cycles	36
Co_3O_4/$NiCo_2O_4$ double-shelled nanocages	~1.0	972 (10 A g^{-1})	92.5 % 12000 cycles	37
$NiCo_2O_4$ nanowires	~1.0	760 (1 A g^{-1})	81% 3000 cycles	38
$NiCo_2O_4$ nanowires–rGO	~10.0	618 (5 mV s^{-1})	Not reported	39
$NiCo_2O_4$ nanoparticles-rGO	~2.5	1222 (0.5 A g^{-1})	91.6% 3000 cycles	40
$NiCo_2O_4$ nanosheets-rGO	~2	835 (1 A g^{-1})	No decay 4000 cycles	41
$NiCo_2O_4$ nanoneedles/graphene	~5	650-400	Not reported	42
$NiCo_2O_4$ nanotubes	Not reported	1647.6 (1 A g^{-1})	93.6% 3000 cycles	43